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High Thermal Conductivity Fibers from PBO

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6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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13. ABSTRACT (Maximum 200 words)

Carbon fibers produced from PBO develop three dimensional ordering that is better than other polymeric precursors, such as PAN. The low electrical resistivities achieved by PBO-based carbon fibers implies high thermal conductivity. Stabilization of the polymer fiber is not needed to obtain the 3-D ordering and low electrical resistivity. This ability to develop into a high thermal conductivity fiber without stabilization may be particularly attractive for use in carbon-carbon composites. The elimination of one carbonization cycle in the manufacture of CC composites may reduce the production cost.

14. SUBJECT TERMS



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FY97 End of Fiscal Year Letter
(01 Oct 1996 - 30 Sept 1997)

ONR CONTRACT INFORMATION

Contract Title: HIGH THERMAL CONDUCTIVITY FIBERS FROM PBO

Performing Organization: Clemson University

Principal Investigator: Dan Edie
[Ph. (864) 656-3056, FAX (864) 656-0784]

Contract Number: N00014-94-1-1159 (CU REF: 05-5911)

R & T Project Number: ccassrt---01

ONR Scientific Officer: A. K. Vasudevan

A. Research Goals

The objective of the project is to examine the conversion of poly p-phenylenebenzobisoxazole (PBO) to carbon fiber and possible use of PBO in carbon/carbon composites. Because of the aromatic, rigid-rod backbone PBO, these fibers can be directly converted to highly graphitic carbon fibers with no prior stabilization. Because of this structure, carbonized PBO fibers should exhibit relatively high thermal conductivities. The goal of the project is to form low-cost, high thermal conductivity carbon/carbon composites by combining PBO fiber with highly carbonaceous matrices which also can be directly carbonized.

B. Significant Results

During this past year, PBO fibers were combined with carbonaceous matrix precursors and formed into CC composites using a single carbonization step. Three different matrix materials were evaluated: a phenolic resin, an alumina-loaded phenolic resin, and a coal tar pitch. In the first series of tests, PBO fibers were coated with the phenolic resin using a powder coating method and a suspension coating method. Then, the coated fibers, or towpreg, were wrapped on a fiber mandrel, forming unidirectional specimens. Finally, the unidirectional specimens were placed in a heated press and consolidated at 1100°C into unidirectional CC composites. The objective of this series of tests was twofold: (i) determine the void content and crack pattern for this fiber/matrix combination and (ii) determine which of the two coating methods produces the more consistent CC composite.

Several of the CC composites formed using each of the coating methods were cross-sectioned, mounted and polished to determine the degree of interfacial bonding. Optical inspection of all samples revealed few cracks or voids at fiber/matrix interfaces, indicative of strong fiber-matrix bonding. This may have been the result of simultaneous shrinkage during carbonization or interaction between the PBO fiber and the phenolic resin prior to, or during carbonization. As expected, numerous small voids and cracks, created the evolution of gases during composite carbonization, could be observed throughout the matrix. However, because of the strong interfacial bonding, the samples also developed cracks perpendicular to the fiber direction to relieve accumulated stresses created during carbonization.

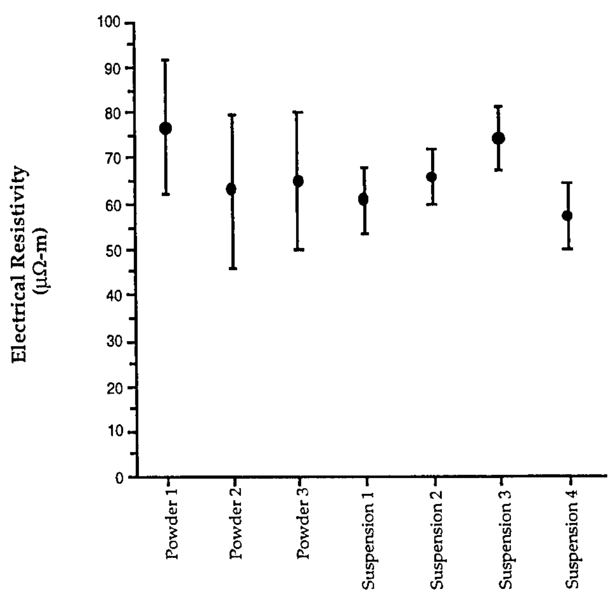


Figure 1: Comparison of carbonized PBO/phenolic carbon/carbon composites by coating method

The average electrical resistivity as well as the range of measured values for thirty CC composite specimens prepared by these two coating techniques (using the same nominal process conditions) are shown in Figure 1. As the figure shows, the suspension coating method produced CC composites with more consistent electrical resistivities. Because of this, the suspension coating method was used in all subsequent experiments. It should be noted these electrical resistivities, measured parallel the fiber axis, were greater than expected. These high resistivities apparently were caused by the stress cracks perpendicular to the fiber axis. Such a crack pattern inhibits the flow of current, and thus, the flow of heat. Obviously, this type of cracking must be minimized if the thermal properties of the CC are to be maximized.

To address this issue, a second series of CC samples were prepared and tested. These samples were prepared by evenly mixing 10 μm in diameter alumina powder particles throughout the phenolic resin, applying this mixed matrix to the PBO fiber using the suspension coating technique, and then thermoforming the coated tows into unidirectional CC composites. The alumina powder was added to create additional interfaces (alumina-phenolic) which could relieve residual stresses during carbonization. The objective was to decrease the size of the matrix cracks. Surprisingly, this alternate stress-release mechanism appeared to reduce not only the size of the cracks, but also the amount of matrix cracking. These smaller stress cracks caused a decrease of the resistivity of the carbonized composites (see Figure 2).

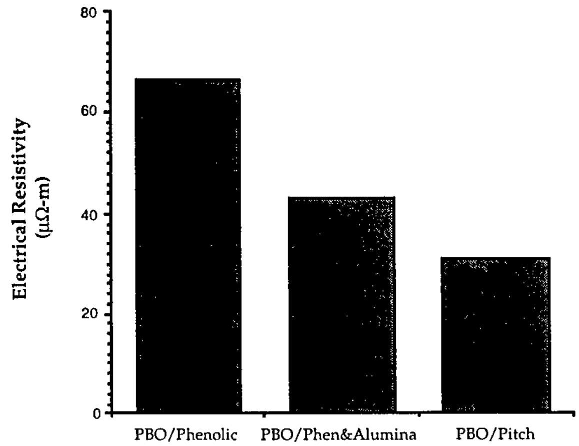


Figure 2: Comparison of carbonized composites containing PBO fibers with different matrices

In a third series, PBO fibers were coated with a coal tar pitch using the suspension coating method and thermoformed into CC composites. Here the objective was to use a highly carbonaceous matrix precursor to decrease void formation during carbonization and, possibly, reduce the amount of interfacial bonding by using a matrix material which is less likely to interact with PBO during carbonization. Again the CC specimens were mounted, cross-sectioned, polished, and inspected to determine the degree of interfacial bonding. Optical inspection revealed that this fiber/matrix combination resulted in enough interfacial cracking to effectively eliminate the stress cracks perpendicular to the fiber axes. Because of this, as Figure 2 shows, the coal tar-based CC composites exhibited lower resistivities than either the phenolic-based or the alumina/phenolic-based carbon/carbon composites.

C. <u>Future Research</u>

The thermal conductivity of all carbon-carbon composites will be measured, and a predictive model for the thermal conductivity of CC will be developed.

D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

"Factors Limiting the Tensile Strength of of PBO Fiber," J. A. Newell and D. D. Edie, *Carbon*, **35**, pp. 825-832 (1997).

2. Non-Refereed Publications and Published Technical Reports

"High Thermal Conductivity Carbon/Carbon Composites Made From PBO-Based Carbon Fibers," C. M. Mundt and D. D. Edie, **Carbon 97**, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 540-541 (1997).

"Viscoelastic Behavior of Air-Blown Pitches," O. Fleurot R. Menendez, C. Blanco, R. Santamaria, J. Bermejo and D. D. Edie, **Carbon 97**, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 190-191 (1997).

"The Influence of Thermal Treatment on the Rheology of Coal Tar Pitches," R. Menendez, J. Bermejo, O. Fleurot and D. D. Edie, **Carbon 97**, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 204-205 (1997).

3. Presentations
   a. Invited

"Preparation and Structure of High Thermal Conductivity Carbon Materials," Gordon Research Conference on Hydrocarbon Resources, Ventura, California, January 12-17, 1997.

   b. Contributed

"Transient and Steady Shear Behavior of Carbonaceous Mesophase," O. Fleurot and D. D. Edie, 1996 AIChE Annual Meeting, Chicago, Il, November 10-15, 1996.

4. Books (and sections thereof)

"Spinning of Carbon Fiber Precursors", Dan D. Edie, John J. McHugh, and James A. Newell, in *The Science of Carbon Materials*, Harry Marsh, ed., Elsevier Science Ltd., in press.

E. LIST OF HONORS/AWARDS

| Name of Person Receiving Award | Recipient's Institution | Name, Sponsor and Purpose of Award |
|---|---|---|
| Dan D. Edie | Clemson University | Elected Chairman of the American Carbon Society |
| Dan D. Edie | Clemson University | Invited to Present Plenary Lecture at the 23rd Biennial Meeting of the American Carbon Society |

F. Participants

Chad Mundt, currently a Ph. D. candidate in Chemical Engineering and should graduate from Clemson University in May, 1998.

G. Other Sponsored Research During Grant Period

This Grant

"High Thermal Conductivity Fibers from PBO," Sponsored by ONR, 0% of time, $30,392/yr, 7/31/94 to 8/1/98.

Other Grants

Development of High Thermal Conductivity Ribbon Shaped Fibers and Evaluation of Chemical Pitch Precursors," Sponsored by ONR, 30% of time, $566,658/yr, 12/31/95 to 4/30/99.

"Fiber-Matrix Bonding and Physical Properties of C/C Composites," National Science Foundation, 0% of time, $11,055/yr, 9/1/96 to 8/31/99.

"Supercritical Extraction for High Thermal Conductivity Fibers," Sponsored by DEPSCoR, 15% of time, $100,000/yr, 9/1/94 to 8/31/98.

H. SUMMARY OF FY97
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/PARTICIPANTS
(Number Only)

| | | ONR | non ONR |
|---|---|---|---|
| a. | Number of Papers Submitted to Referred Journal but not yet published: | 0 | 3 |
| b. | Number of Papers Published in Refereed Journals: | 1 | 3 |
| c. | Number of Books or Chapters Submitted but not yet Published: | 1 | 0 |
| d. | Number of Books or Chapters Published: | 0 | 0 |
| e. | Number of Printed Technical Reports & Non-Referred Papers: | 3 | 4 |
| f. | Number of Patents Filed: | 0 | 0 |
| g. | Number of Patents Granted: | 0 | 0 |
| h. | Number of Invited Presentations at Workshops or Prof. Society Meetings: | 1 | 3 |
| i. | Number of Contributed Presentations at Workshops or Prof. Society Meetings: | 0 | 1 |
| j. | Honors/Awards/Prizes for Contract/Grant Employees: (selected list attached) | 2 | 0 |
| k. | Number of Graduate Students and Post-Docs Supported at least 25% this year on contract grant: | 1 | 5 |
| | Grad Students: TOTAL | 1 | 5 |
| | Female | 0 | 1 |
| | Minority | 0 | 0 |
| | Post Doc: TOTAL | 0 | 0 |
| | Female | 0 | 0 |
| | Minority | 0 | 0 |
| l. | Number of Female or Minority PIs or CO-PIs | | |
| | New Female | 0 | 0 |
| | Continuing Female | 0 | 0 |
| | New Minority | 0 | 0 |
| | Continuing Minority | 0 | 0 |

Enclosure (4)